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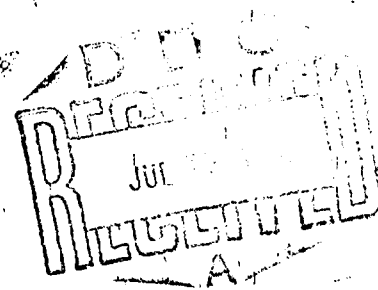## Factors Governing the Storage Life of Solid Propellant Rocket Motors

R Stenson

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Propellant Rocket Motors

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motors on storage is reviewed and the problems of safety and
deterioration in performance are considered with emphasis on
the basic chemical and physical changes involved. Storage at
elevated temperatures is shown to be very important and accel-
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materials, temperatures of ignition, estimation of the rate of
stabiliser consumption and its relation to the Safe Chemical
Life, and measurement of heat evolution to permit calculation
of cook-off limitations on charge dimensions for double-base
or similar reactive propellants. Changes in motor performance
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formation due to chemical decomposition within double-base or
"exotic" propellants and from interactions of propellant
ingredients with other motor components such as thermal
insulants, inhibitors and adhesives. Changes in burning rate,
and rheological problems associated with usage over a wide
temperature range are included. The problems of plasticiser
migration are described in a separate paper with special
reference to cellulose acetate and ethyl cellulose inhibitors.

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FOREWORD

This paper by Dr R Stenson was originally written for the
Annual Meeting of the Institut für Chemie der Treib-und
Explosivstoffe held at Karlsruhe in September 1971.

This paper is now reproduced as an ERDE Technical Note in
order that somewhat wider circulation can be given.

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1   SUMMARY

The behaviour of composite and double-base propellant rocket motors on storage is reviewed and the problems of safety and deterioration in performance are considered with emphasis on the basic chemical and physical changes involved. Storage at elevated temperatures is shown to be very important and accelerated testing is used to predict the effects of much longer cool storage. Tests necessary to avoid eventual spontaneous inflammation include compatibility of ingredients and materials, temperatures of ignition, estimation of the rate of stabiliser consumption and its relation to the Safe Chemical Life, and measurement of heat evolution to permit calculation of cook-off limitations on charge dimensions for double-base or similar reactive propellants. Changes in motor performance are described, in particular rupture of the charge by gas formation due to chemical decomposition within double-base or "exotic" propellants and from interactions of propellant ingredients with other motor components such as thermal insulants, inhibitors and adhesives. Changes in burning rate, and rheological problems associated with usage over a wide temperature range are included. The problems of plasticiser migration are described in a separate paper with special reference to cellulose acetate and ethyl cellulose inhibitors.

2   INTRODUCTION

The storage characteristics and Service Lives of rocket motors are assessed in the UK by the Ordnance Board, which is a separate authoritative body charged with the duty of advising on the safety and effectiveness of all armament proposed for use in the British Services. To this end it is called upon to organise qualification or acceptance trials designed to test whether new weapons conform in detail with the requirements laid down by prospective users. The Board, which is largely composed of officers from the Armed Services who are the ultimate users of the weapons, seeks detailed advice at all times from the many specialists in the field and publishes the results of its deliberations in Proceedings. Over the years it has built up an enviable reputation for objectivity, accuracy and thoroughness. This paper does not, however, cover the behaviour of rocket motors in Ordnance Board trials and the consequent environmental limitations, but rather describes some of the background expertise that is available to this Board in UK research establishments.

A solid propellant consists of a mixture of oxidiser and fuel. The oxidiser can be crystalline and embedded in a fuel matrix, which may be a viscous liquid or a rubbery polymer eg polyisobutene, polyurethane, carboxy-terminated polybutadiene. Alternatively, the oxidiser and fuel can be present in the same molecule as in double-base propellants containing nitroglycerine and nitrocellulose. These propellants are associated in rockets with a range of materials which are used to limit the burning surface, provide heat insulation to the motor body, relieve stresses, retain the propellant, house igniters etc. The interaction between these materials and the propellant, and changes in propellant properties during shelf or Service

storage for a number of years may result in changes in the motor performance parameters, its physical ability to withstand environmental conditions, or more catastrophically affect its safety in storage or functioning. This report gives separate consideration to safety, of major interest with propellants containing nitrocellulose, nitroglycerine, or other reactive compounds, and to the various types of change in performance.

3 SAFETY

There must be no possibility of spontaneous inflammation under storage or usage conditions. The two main areas of concern are how long is the charge likely to be storable safely at elevated temperatures (the Safe Chemical Life), and also whether self heating is likely to occur when larger charges are involved.

3 1 Safe Chemical Life

Nitric esters (and some other ingredients used in propellants) are inherently unstable and are continually undergoing slow decomposition even at ambient temperatures. Products of decomposition (nitrogen dioxide, nitrous and nitric acids) catalyse reaction unless they are removed by stabilising additives, a variety of which are available. The traditional carbamite (diphenyl diethyl urea) used in double-base propellants, although effective, has now been largely superseded since it reacts and produces gases which are not absorbed by the propellant matrix and cracking may occur eventually. The stability of double-base propellants and compatibility with new ingredients and inhibitors are assessed by determination of the stabiliser consumption, and in addition by measuring the evolution of gas or heat during accelerated storage trials. A concept of Safe Chemical Life for Service usage has evolved, which is related conventionally to the quantity of stabiliser present. The Safe Chemical Life at a given storage temperature has usually been standardised, for carbamite-stabilised propellants as the time for half the stabiliser in the propellant to be consumed. Reliable estimates are obtained provided accurate methods of analysis are available eg thin layer chromatography, to monitor the stabiliser concentrations. Prediction of the Safe Chemical Life under normal storage conditions is obtained by advance information derived from storage at elevated temperatures. Care must be taken that the selected temperature is not so high that it introduces unusual reactions and, at present, tests are usually performed at 50 or $60^{\circ}C$. In the UK the Safe Chemical Life is then equated to years at $32^{\circ}C$ ($90^{\circ}F$) by the use of a temperature correction factor of 2.9 for every $10^{\circ}C$. The figure required is generally at least 7 to 10 years for rocket charges and 20 to 30 years or longer for gun propellants (see Table 7).

Other tests for Safe Chemical Life, particularly to screen new ingredients and materials for compatibility, are utilised. Gross incompatibility is shown by the simplest of tests and strong evidence for rejection of a particular new ingredient or material is available quickly. Very often, however, exhaustive and painstaking examination is necessary to prove a system acceptable if the behaviour is complex and the evidence not straightforward. In the Silvered Vessel Test a finely divided standard propellant containing minimum stabiliser,

is mixed with a test material and heated at 80°C in a vacuum flask (Dewar silvered vessel) until fuming or a 2°C temperature rise is observed as the sample self heats. Results are quoted in days and a reduction of more than 20 per cent in SV figure, when compatibility is being tested, is regarded as indicative of a poorly compatible material which should not be used if any access to propellant ingredients (such as nitroglycerine) is possible. A 95°C test has been instituted for rapid screening and consists of measuring the time to ignition, or obvious decomposition at 95°C of cubes of propellant, side 12 mm, wrapped in aluminium foil. Other quick tests such as the Methyl Violet Test, the Abel Heat Test at 60 to 82°C, or the 105°C weight loss test are used to show initial quality for special types of nitrocellulose propellant. These tests are regarded as guide lines only and formal reliance is placed upon residual stabiliser analysis.

Future developments may include the application of thermo-chemical methods to stability assessment since a very early indication of incipient chemical decomposition at fairly low test temperatures may be possible. Heat flow calorimetry is a promising technique under development both in the UK and in Holland in which sensitive detection devices are used to measure heat generated by propellants undergoing slow decomposition. Differential scanning calorimetry has also been adapted and the presence of incompatible materials is indicated by a sharp exotherm at temperatures well below that characteristic of a conventional double-base propellant.[1]

Composite propellants contain ingredients, particularly binders, which are generally more stable than nitric esters, and consequently greater chemical life is conferred on the propellants. However, the necessity for anti-oxidants and "stabilisers" in some rubber propellant formulations suggests that the principles of stabiliser consumption might be usefully applied. The general levels of thermal stability to be expected from the various types of common ingredients and propellants are indicated by the conventional Ignition Temperature Test in Table 1. The advantage of composite propellants in this respect is shown. If smokeless exhausts are essential, however, then the lower thermal stability of nitric ester based propellants must be accepted.

TABLE 1

Ingredient	Ignition Temperature °C (Heating Rate 5°C/min)
Nitrocellulose	170
Nitroglycerine	160
Double-Base Propellant	160 – 170
Ammonium Perchlorate	400
RDX	210
HMX	260
Composite Propellants	250 – 300

Modern double-base stabilisers normally permit a long Safe Chemical Life so that it is now found that factors affecting performance are more likely to limit the useful Service life. For composite propellants under similar storage conditions the most critical factor is more likely to be mechanical deterioration. These aspects are covered in Section 4.

Aerodynamic heating due to external carriage on high speed aircraft poses special problems and much greater thermal stability may be required; these special propellant requirements are not discussed in this paper. Even where double-base propellants would be considered safe by standard criteria, an additional hazard may exist if the motor design permits severe temperature gradients and enables nitroglycerine to distil from the hot propellant and condense onto a nearby cold surface.

3 2   Self-Heating

When used in large charges it is possible for double-base propellants to ignite spontaneously at storage temperatures below the nominal ignition temperature and within the 'Safe Chemical Life'. The slow spontaneous decomposition of this type of propellant causes heat evolution. For example, a typical double-base propellant would liberate about 7×10^{-6} cal*/g s at $20°C$ and 4×10^{-4} cal/g s at $110°C$. These figures fit the equation $H = 10^{17.38}$ exp $(-36,400/RT)$ cal/g s. The rate of production of heat is roughly trebled for each $10°C$ rise in temperature. The generation of heat by chemical reaction is proportional to the mass of propellant but loss of heat occurs only from the surface, the area of which is proportional to $(mass)^{2/3}$. Hence the larger and more compact the mass, the larger is the thermal gradient required, between the middle and the outside, to dissipate the heat. This extra temperature at the centre of the propellant mass enhances the heat evolution and when the mass/temperature are large enough thermal instability and cook-off will ensue. The calculation of "cook-off" conditions involves measuring the rate of production of heat with temperature, the specific heat, and thermal conductivity of the propellant. The critical radius of a solid cylinder of propellant above which the steady state flow of heat no longer applies, so that there can be self-ignition, is given by the equation:

$$a^2 = \frac{2K}{dA} \frac{RT^2}{E} \exp\left(\frac{E}{RT}\right)$$

where a = Radius of cylinder in cm

K = Thermal conductivity of propellant and is of the order of 5.5×10^{-4} cal/cm s $°C$

T = Storage temperature $(°K)$

E = Activation Energy 36,400 cal/mole

d = Density of propellant 1.55 g/cm^3

A = Constant $10^{17.38}$ cal/g s

R = 1.937 cal/mole $°K$

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*1 calorie = 4.187 joules

The time to ignition is then given by:

$$t(min) = \frac{c}{A} \frac{RT^2}{E} \exp\left(\frac{E}{RT}\right)$$

where c = specific heat of propellant, taken to be 0.357 cal/g °C in this case.

Theoretical predictions of critical sizes and times to self-ignition for a simple double-base propellant are given in Table 2.

TABLE 2

Temp °C	Theoretical	
	Critical Cylinder Diameter (mm)	Time to Cook-off (h)
80	514.5	105
105	83.3	3.3
110	61.3	1.7
114	49.0	1.0
120	34.3	0.5

Early experimental checks at 110°C indicated that the calculated sizes for self-ignition were on the high side, whilst observed times for ignition were about three times expected values. Recent tests have been conducted on sections of a simple tubular double-base propellant charge and temperature differentials were monitored by thermocouples mounted in the centre of and outside the charge. Below 105°C even degraded propellant would not cook-off although such material was converted to a sticky mass which would be quite unserviceable long before the end of the four weeks testing. The difference in temperature between thermocouple records was no more than 1°C. There was a critical temperature of 112°C above which propellant cooked off readily (the predicted critical temperature was 110°C). Thermocouples showed a difference of 3°C for several hours before a 4 to 5°C difference occurred at the onset of the runaway part of the self-heating. Between 105 and 112°C cook-off occurred only after considerable decomposition of the propellant.

Tests are difficult to correlate with theory since the warming up period in normal thermostats can be a considerable fraction of the time to cook-off. Instantaneous heating to the reference temperature never occurs in real situations encountered in Service, where the prime consideration is frequently the time required for sufficient heat to be conducted to the propellant from the environment. Agreement with theory is considered reasonable for smaller

sizes in view of the difficulties in determining accurate experimental data for the above equations, and in addition the complications that exist of degradation of the propellant and reduction of thermal conductivity caused by cracks produced by gas accumulation. It is indicated later that gas cracking is likely to precede cook-off so that there would be considerable violence when a fissured charge cooked-off.

4   CHANGES IN PERFORMANCE

Changes in performance may arise from chemical or physical causes and these are examined separately. The effects produced can be catastrophic if storage results for example, in loss of integrity of the propellant charge or in the inhibition/thermal insulant bonding, or merely undesirable or unacceptable owing to changes in burning characteristics.

CHEMICAL CAUSES

4.1   Cracking Due to Gas Accumulation

Chemical decomposition and interaction within double-base or newer propellants containing "exotic" and reactive ingredients can cause gas evolution. The theoretical considerations below have involved double-base propellants but can be applied, after relevant parameters have been determined to newer "exotic" systems. The gas evolution is accelerated on raising the temperature and as a result an internal gas concentration is set up and unless the gas can diffuse away through the propellant at a rate faster than it is produced, eventually the pressure in equilibrium with the dissolved gas may exceed the strength of the propellant and result in internal cracks being developed. It is assumed that gas can first come out of solution where there are nuclei such as chalk, oxidiser or ballistic additive crystals. The balance of forces across the diameter of a bubble can be considered to correlate critical pressure p_c and tensile properties of the propellant under long times of loading. A simplified formula for hard propellants is:

$$p_c = \frac{2T}{(1 + 2\phi)}$$

where T =   long term tensile strength
        ϕ =   elongation at break

Rosser (classified publication) measured directly the pressure generated in double-base propellant on hot storage at 60°C in a charge 106 mm dia by 114 mm long clamped between two steel plates. A mercury capillary manometer was fitted with appropriate precautions into a 1.5 mm hole drilled 50 mm deep into the base of the charge. The pressure generated during storage was calculated from the compression of the air in the sealed limb of the capillary. Maximum pressures of 350 kN/x^2 (gauge) were developed after six to ten weeks.

To calculate the theoretical maximum pressure the rate of gas evolution must be measured. Rosser et al found that for double-base propellant it is about 0.0005 v/v propellant/h at 60°C. The composition of the gas depends upon the nature of the propellant ingredients, the decomposition mechanism and side reactions. The rate of gas escape depends upon the solubility of the gases evolved in the propellant matrix and their respective diffusion constants. The rate of gas escape can be assessed by measuring the permeability of the propellant to various gases in the laboratory. By equating the rate of gas formation and escape for a steady rate Rosser calculated the maximum pressure developed for a given storage temperature. Along the axis of a cylinder the maximum pressure

$$P_{max} = \frac{Q \, da^2}{4F} + 760 \text{ mmHg}$$

where F is the gas permeability, Q is the rate of gas evolution/g, d is the density of the propellant and a is the radius of the charge. Considering the simplifying assumptions made, reasonable agreement between theoretical and observed pressure developed was obtained.

Ward[2] developed a mathematical treatment based on Fick's Law of Diffusion giving the rate and extent of pressure development in propellants of different shapes. If Q is the mass of a particular gas produced in g/s g of propellant, then

$$Q = Ae^{-\frac{B}{RT}}$$

where B is the activation energy for the rate-determining step by which the gas is produced. A and B may be found from a plot of log Q against $\frac{1}{T}$.

If C is the concentration of gas in g/ml of propellant, then according to Henry's law C = kp where k is the solubility and p is the partial pressure. It is assumed that it is obeyed reasonably well for gas solubility in propellants, so that calculated gas concentrations can be converted to gas pressures.

The equation for diffusion is

$$P = -D \frac{\delta C}{\delta X}$$

where P is the quantity of gas in grams passing 100 mm^2 of surface/s normal to the gradient of concentration $\frac{\delta C}{\delta X}$ and D is the diffusion constant. Diffusion is generally an activation process so D = $D_o e^{-B'/RT}$.

The fundamental diffusion equation under isothermal conditions can then be derived for the change in gas concentration with time at a given storage temperature.

$$\frac{\delta C}{\delta t} = D \left[\frac{\delta^2 C}{\delta x^2} + \frac{\delta^2 C}{\delta y^2} + \frac{\delta^2 C}{\delta z^2} \right] + Q' \qquad (1)$$

where Q' = Qd the mass of gas generated/s ml of propellant. The general solution of this equation for non-equilibrium conditions with intervention of cracking is complex and reference should be made to Ward's original paper. Two limiting situations are relatively simple:

a   Where the propellant cracks due to excessive gas accumulation before diffusion can become significant. In this case $\delta C = Q' \delta t$ since the gas concentration in the central region of the charge is independent of its size, provided the latter is large.

b   Where equilibrium is reached between the rate of gas formation and escape by diffusion with a maximum concentration less than the critical value for crack formation. For the stationary state $\frac{\delta C}{\delta t} = 0$. This applies to all charges below a certain critical size.

The stationary state equation has been applied to slabs and this is given in some detail. Other shapes such as infinite cords, spheres, tubes both loose and case-bonded are also considered.

   1 Slab of Propellant

Consider propellant infinite in yz directions and $2a$ thick in x direction. For a steady state $\frac{\delta C}{\delta t} = 0$ and Equation 1 gives

$$\frac{D d^2 C}{dx^2} = -Q'.$$

Integrating $D \frac{dC}{dx} = -Q'x + \text{constant.}$

Now $\frac{dC}{dx} = 0$ at $x = a$

$\therefore \ D\frac{dC}{dx} = Q' (a - x).$

Integrating again $DC = Q'(ax - \frac{x^2}{2}) + \text{constant.}$

When $x = 0$ or $2a$ at the boundary $C = J$
(gas concentration at the boundary)

$\therefore \quad C = \frac{Q'}{D} (ax - \frac{x^2}{2}) + J.$

The distribution of concentration is parabolic with x. The maximum concentration is at $x = a$

then $C_{max} = \dfrac{x^2}{2D} + J.$

When $J << C_{max}$

$$C_{max} = \frac{Q'a^2}{2D} .$$

Similar formulae were derived by Ward for common propellant charge shapes.

ii   Infinite Cord

$$C_{max} = \frac{Q'a^2}{4D} + J \qquad radius = a$$

iii   Sphere

$$C_{max} = \frac{Q'a^2}{6D} + J \qquad radius = a$$

iv   Tubular

Lawson (classified publication) has derived an expression for a tube with a small hole:

$$C_{max} = \frac{Q'a^2}{4D} \left\{ 1 - (1 + \log \log (\tfrac{a}{b})^2)/\log (\tfrac{a}{b})^2 \right\} + J,$$

where $\quad \dfrac{a}{b} = \dfrac{\text{outer radius}}{\text{inner radius}} .$

The expression outside the brackets is the value of C_{max} for a cord of the same external diameter. Comparisons for cords and tubes of equal external diameters are given in Table 3.

TABLE 3

$\dfrac{a}{b} = \dfrac{\text{Outer radius}}{\text{Inner radius}}$	$\dfrac{C_{max}\ \text{tube}}{C_{max}\ \text{cord}}$
3	0.25
5	0.34
20	0.53
400	0.71
8,000	0.79

It is concluded that a very tiny hole in the centre of the cord will reduce the gas pressure by about 20 per cent over the solid cord.

v Case-Bonded Tube

Lawson derived for a case-bonded tube:

$$C_{max} = \frac{Q'a^2}{4D}\left\{ \log_e \left(\frac{a}{b}\right)^2 - 1 + \frac{1}{\left(\frac{a}{b}\right)^2} \right\} + \omega.$$

Table 4 indicates that the tendency to crack increases rapidly with increase in the radius ratio. For a typical loading density with a propellant occupying about 85 per cent of the space within the outer tube of a high performance central conduit rocket, the ratio $\frac{a}{b} = 2.6$. The maximum pressure, and thus the tendency to crack, is about the same as for a cord of the same external diameter. This might rule out prolonged hot storage (49°C or above) of very large motors of this type containing double-base propellants since critical diameters are seldom above 305 mm at 49°C nor lives above a few months at this temperature in sizes larger than the critical size.

TABLE 4

$\frac{a}{b} = \frac{\text{Outer Radius}}{\text{Inner Radius}}$	$\dfrac{C_{max} \text{ for case bonded tube}}{C_{max} \text{ for cord of same diameter}}$	Size of equivalent cord
1.65	0.37	0.61a
2	0.63	0.80a
3	1.31	1.14a
4	1.83	1.38a
6	2.61	1.62a
10	3.60	1.90a

4 1 1   Critical Size and Temperature

It follows from the above analysis that propellant web thickness and temperature both affect the onset of cracking. At a given temperature there are two critical sizes corresponding to conditions (a) and (b), or for a given charge size there are two corresponding critical temperatures, a lower one below which the gas can escape before developing a critical pressure and where cracking rarely occurs, and is possible only after the mechanical properties have degraded on long hot storage, and an upper temperature above which diffusion can be ignored and the time to develop cracks is independent of size.

The lower theoretical critical thickness can be expressed for a sphere as follows:

$$C_{max} = \frac{Q^1 a^2}{6D}$$ where a is the critical radius and C_{max} is the gas concentration for cracking to appear.
Let $C_{max} = C_{crit}$.

$$\therefore \quad C_{crit} = \frac{Ae^{-\frac{B}{RT}} \cdot a^2 d}{6D_o e^{-\frac{B^1}{RT}}}$$

$$\therefore \quad a^2 = \frac{6D_o C_{crit} e^{(\frac{B - B^1}{RT})}}{Ad}$$

$$\ln a = \tfrac{1}{2}\ln \frac{6D_o C_{crit}}{Ad} + \tfrac{1}{2}\left(\frac{B - B^1}{RT}\right).$$

An approximation can be made by assuming that changes in C_{crit} can be neglected over the temperature range considered, in comparison with the exponential term,

when

$$\frac{6D_o C_{crit}}{Ad} = K$$

then

$$\ln a = \tfrac{1}{2}\ln K + \tfrac{1}{2}\left(\frac{B - B^1}{RT}\right).$$

Having determined the critical size at one temperature it is possible by the above equation to estimate values for other temperatures. An estimate of $B - B^1$ can be made by measuring gas evolution and diffusion or gas permeability at various temperatures; K can then be deduced for one temperature. In practice it is easier and more accurate to determine the critical size at the required temperature in view of the experimental difficulties and uncertainties in gas evolution, diffusion and permeability measurements.

In a widely accepted UK cracking test, four 51 mm cubes of the propellant are stored in a 0.8 mm thick aluminium can in an oven, the temperature of which is maintained at $80° \pm 0.5°C$. Each aluminium can has a loose-fitting cover secured by tape. The development of porosity or cracks in the cubes during hot storage is followed by X-ray inspection of the canned cubes. The cubes

are X-rayed before being placed in the oven and thereafter daily during the first week on test and subsequently every other day until cracks are detected. The time during which the cubes are out of the oven for inspection does not exceed ten minutes, corresponding to a maximum temperature drop of 12°C at the centre of the 51 mm cube. Experiments proved this brief temperature drop to have an insignificant effect on the cracking life of the propellant. Storage using larger, or smaller sized cubes and different temperatures of storage is necessary to bracket critical thicknesses. Cracking results for double-base propellants are somewhat variable and this is thought to be due to small amounts of impurity.

Some typical critical sizes for given storage temperatures are given in Table 5. Propellant A refers to a simple system and B to a high performance propellant.

TABLE 5

Propellant	Temperature (°C)	Critical Thickness (mm)		
		Lower	Upper	Days to Crack
A	50 60 80	47 22 5	93 47 12	85 25 2
B	50 60 80	300 170 60		

Some ballistic modifiers tend to increase the rate of gas evolution which results in a reduced critical thickness although a few modifiers can be selected which are not deleterious. Those adopted for propellants in Service use must confer desirable ballistics, but also must not introduce cracking problems.

Ideally the use of a specific propellant in a large boost and particularly in a large sustainer necessitates the web thickness to be less than the critical thickness for the highest storage temperature envisaged. Cracking can be the determining factor in the storage life of double-base propellants as shown later in Table 7.

The above refers specifically to double-base propellants but similar treatment is applicable to any propellant which contains reactive ingredients giving gaseous products. Composite propellants containing chemically inert ingredients are free from this problem but the addition of nitro compounds

can raise the problem acutely if the rate of gas evolution is say more than 0.0005 vol gas/vol propellant/h at 80°C. This treatment relates to gassing within the propellant but complications can arise with inhibited loose charges or thermally insulated motor designs employing case bonded charges (see Section 4 4). For the loose charge both the inhibitor and the adhesive used must be permeable to propellant decomposition gases. Highly cross-linked adhesives and thermosetting potting inhibitors have on occasion not allowed sufficient diffusion of gases and pressure has eventually built up to cause either blistering of the inhibitor, extensive unbonding or cracking. For case-bonded charges the permeability of the inhibitor system is not of concern but even slight incompatibility may produce a local gas concentration at the insulant/propellant interface which is sufficient to cause premature cracking or unbonding. It is also desirable that the bond strength should be no less than that of the propellant itself, since the concentration of dissolved gas is a maximum in the propellant next to the impermeable wall of the rocket motor case.

4 2 Ballistic Changes

Many rockets have specifications requiring fairly close control of ballistics, so it is necessary to ensure that the propellant does not change its energy level or burning rate very much on prolonged sto e. Accelerated hot storage tests are used to check new propellants, nich should show only small changes in 3 to 6 months at 60°C, but prolonged storage at more normal temperatures is still required for final acceptance.

Changes in energy due to the slow decomposition of double-base propellants are usually negligible over the storage life of a rocket charge. Larger changes can occur due to changes in volatile matter (eg water) or loss of plasticisers, if rockets are badly sealed. Thus a typical dry double-base propellant will burn about five per cent faster than one containing one per cent of water. Water is also deleterious in most composite propellants.

The most serious changes are met in propellants containing ballistic modifiers if these are volatile or chemically reactive. Nitration of modifiers in double-base propellants has been demonstrated in some cases, with associated changes in burning rate. Microscopic examination of thin sections of double-base propellant has shown in one case a birefringent constituent which is thought to be formed by hydrolysis of the ballistic modifier with possible further reactions with propellant ingredients.

4 3 Mechanical Deterioration

This may be caused by either physical change (see Section 4 5) or by chemical reaction. Degradation of the propellant on storage by chain-breaking of the polymer binder and reaction of the fuel/oxidiser mixture inevitably affects mechanical properties. In the case of double-base propellants it is thought that deterioration in mechanical properties will continue to be a much more serious limitation than the Safe Chemical Life on the life of rocket charges which are subjected to high stresses on firing. For example the "Physical Life" of a typical simple double-base propellant is about one third to one half the Safe Chemical Life. At the end of this time, the strength and

Young's modulus of the propellant may be only about half the original values so that there is no longer an adequate factor of safety at the upper temperature limit. The temperature coefficient of mechanical degradation is about 3.0 for 10°C. The dilute solution viscosity in n-butyl acetate solution can be used to follow the early stages in the degradation of nitrocellulose and nitrocellulose propellants. A viscosity change exceeding about 30 per cent marks the onset of serious mechanical degradation.

TABLE 6

Temperature (°C)	Time Stored (months)	Intrinsic Viscosity (η_I)	Degradation (per cent)
60	0	2.04	-
	$1\frac{1}{2}$	1.63	20
	4	1.63	20
	12	1.27	38

The example given in Table 6 indicates that the mechanical properties of the propellant will not withstand 1 year at 60°C without considerable deterioration, but it must be remembered that the relationship between intrinsic viscosity and mechanical properties of the propellant is no more than qualitative.

Some composite propellants are susceptible to mechanical deterioration which is frequently the most severe limitation on storage life. Thermal instability of the binder in the presence of a strong oxidiser such as ammonium perchlorate results in softening of the propellant and may limit the maximum storage temperature. Post-cure hardening by crosslinking of thermosetting binders may also occur. Hydrolytic instability of the binder or binder/oxidant may also necessitate the sealing of rocket motors. Moisture can also cause lack of adhesion at the oxidiser/binder interface. Age-hardening of highly filled composites is also a well known phenomenon. It is not well understood and is probably due to a combination of physical and chemical causes.

PHYSICAL CAUSES

4.4   Introduction

As rocket motors have become more and more sophisticated, more varied materials have been employed. The propellant itself is no longer simple and can contain a number of polymers, crosslinking agents, plasticisers, stabilisers, oxidisers, fuels and ballistic modifiers. The propellant is usually bonded to, or in contact with, one or more of a range of polymeric materials which also may be bonded to the motor wall. Solvents from adhesives

and lacquers may be left in the motor. The fabrication of inhibiting materials may involve the use of volatile prepolymers and reactive cross-linking agents which may not combine completely and remain a source of chemical reactivity. Diffusion to susceptible components such as fuze match-heads may occur where attack could, in extreme cases, cause malfunctioning.

Serious ballistic malfunctioning may occur due to failure of the thermal insulant or inhibitor bond to the propellant charge. Failure is not usually due to chemical degradation of the polymer on hot storage; rubbers, thermoplastics and thermosets of satisfactory stability, with or without the addition of antioxidants, can be selected to withstand the maximum storage temperature environment in the rocket motor in contact with propellant and other components. Resistance to hydrolytic attack is important since water may be present in some propellants. Adhesion failure at the propellant/inhibitor interface may be caused by chemical reaction at the interface, but this is generally a small effect provided the inhibitor selected is truly compatible with the propellant. Bond failure can occur due to a variety of physical causes such as dissimilar mechanical properties of propellant and inhibitor, lack of flexibility of the inhibitor, or separation at the interface due to low gas permeability of the inhibition or adhesive. These types of failure should not occur in Service-accepted motors as they should have been eliminated by accelerated testing during the development of the design and suitable alternative systems devised.

4.5   Rheological Problems

Physical changes in the mechanical properties of double-base propellants can sometimes be ascribed to the method of manufacture since rheological properties are determined not only by the propellant formulation but also by the degree of gelatinisation of the nitrocellulose, homogeneity and the extent of frozen stresses. The examination of the fine structure of cast propellants sometimes reveals hard centres in the casting powder grains which may be gelatinised further by post-curing. The increase in strength of the propellant is achieved at the expense of elongation which, for hard propellants containing high concentrations of nitrocellulose, could lead to ready cracking of the propellant charge. The strength and elongation at break of solvent-extruded propellants are considerably greater than those of corresponding solventless propellants, and advantage may be taken of this in charges having small web thicknesses.

Differential thermal contraction between a case-bonded propellant charge and the rocket tube causes circumferential strains in the propellant at all temperatures below the curing temperature, reaching a maximum at the surface of the conduit, being particularly severe with high loading densities. Long term stressing of double-base propellants may lead to a significant reduction in tensile strength and Young's modulus which is not due to degradation of the polymer. These problems may be aggravated by temperature cycling which may superimpose failure due to fatigue. Double-base propellants which contain non-colloidal fillers are more likely than unfilled ones to fatigue on temperature cycling, and dewetting has to be taken into account. For loose inhibited charges the effect of low temperature depends on the degree of

mismatch of mechanical properties between the inhibitor and the propellant. For a rigid inhibitor the lower temperature of Service use may be limited by bond failure or cracking of the inhibitor. Even if no failure is present before firing, a low temperature ignition shock or rapid pressure build-up may propagate incipient inhibitor failure. Hence cold storage and thermal cycling of simple model rocket charges have been carried out to evaluate various propellants.

Dimensional changes of the propellant can occur on continuous storage of a rocket motor since the weight of propellant causes a steady stress in one direction. An estimate of the maximum size of charge which will withstand gravitational stresses indefinitely, and acceleration stresses on firing, can be obtained by equating the shear modulus of the propellant with the maximum stress in the charge. In the simple case of a long cylindrical charge with central conduit, case-bonded and stored vertically, the stress is a shear, increasing towards the wall of the tube where it is equal to the weight of the charge divided by the area of supporting surface. The vertical deflection at the inner surface can also be calculated. Gravitational loads on solid propellant rocket grains have been considered in detail by Hopkins et al.[3] The UK plastic propellant was tested experimentally since it has a low yield stress and some measurable deformation occurs in a reasonable time with test specimens. Good agreement with theoretical predictions was found.

Double-base propellants and crosslinked composites do not generally suffer from significant slumping and it would be expected that the charge would keep its shape indefinitely. Double-base propellants containing a minimum of nitrocellulose and composite propellants suffering from mechanical deterioration due to polymer breakdown might well deform on high temperature storage. Some dimensional changes of a small order of magnitude will occur for double-base propellant charges on hot storage when relaxation of stresses present on extrusion causes a slight shortening of the charge. In addition thermal expansion of the propellant is much larger than that of steel, light alloy or fibreglass so that charges which are a tight fit when hot will become slack on cooling.

Vibration of the rocket motor does not normally cause severe change but the propellant rheology in relation to the particular application must be carefully studied since instances of breakdown of structure have been experienced.

4. 6   Migration of Plasticisers

A serious problem can be caused by the migration of ingredients within the rocket motor, particularly when the propellant or other components contain low molecular weight ingredients capable of diffusing rapidly under hot storage conditions. Ingredient migration is a particularly difficult problem for double-base propellants where absorption of nitroglycerine by the insulant or inhibitor can not only affect propellant ballistics but at the same time reduce the flame-resistance of the inhibitor. Swelling of the insulant or inhibitor due to plasticiser absorption can occur and cause high stress concentrations at sharp corners with consequent bond failures. The inhibitor may also become mechanically weak and softened due to plasticiser absorption.

Experiments conducted at ERDE to classify migration parameters are described in a separate paper and cover the testing of conventional inhibitors, cellulose acetate and ethyl cellulose, for double-base propellants and the interactions of polymers with nitroglycerine and other propellant ingredients.

5   OVERALL STORAGE CAPABILITY

The foregoing is a summary of the more important storage problems with which the rocket designer and user are confronted. The choice of temperature coefficient to deduce storage life from accelerated testing at elevated temperatures depends upon whether the limiting factors are physical or chemical in nature. Most of the relevant chemical reactions have broadly similar energies of activation so that temperature coefficients are well understood and are of the order of threefold for $10^\circ C$. Occasionally testing at high temperatures gives abnormal reactivity due to some new reaction occurring above a threshold temperature; subsequent conversion to normal climatic temperatures then gives somewhat pessimistic results. Where physical causes are the relevant factors lower energies of activation and temperature coefficients are frequently found.

Table 7 summarises typical overall storage limitations for a simple double-base propellant and shows the significance of size in relation to the different types of failure.

TABLE 7

Temp (°C)	Chemical Life	Cracking of Sheet		Self-Heating		Mechanical Properties Degraded
		Lower Critical Thickness (mm)	Time to Crack	Critical Sphere Radius (mm)	Time to Cook-off	
30	40 years	144	$3\frac{1}{2}$ years	12,740	27 years	$11\frac{1}{2}$ years
60	1 year	22	25 days	1,127	78 days	125 days
80	33 days	4.9	2 days	252	4 days	$10\frac{1}{2}$ days
100	3 days	≈2.5	$2\frac{1}{2}$ hours	66	$6\frac{1}{2}$ hours	-
120	6 hours	-	-	19	≈$\frac{1}{2}$ hour	-

The above simple propellant did not contain ballistic modifiers, but the storage life will be dependent upon the specific ballistic modifier present

and may range from three months to a year or more at 60°C depending on the ballistic design tolerances. The rocket motor will also contain thermal insulants/inhibitors and choice of unsuitable materials may give storage lives at 60°C ranging from two to four weeks to two or three months depending on the extent of plasticiser diffusion. Service lives of some US motors have been quoted recently.[4]

On these principles the storage life of a specific motor design for a given temperature environment can be estimated. Further safeguards on safety and reliability can only be made by accelerated trials on the rocket motor aimed to simulate Service usage. Finally a proportion of motors should be returned from Service use over the years for confirmatory examination so that the predicted and demonstrated Service lives can then be compared.

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7   ACKNOWLEDGEMENT

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